SINTERING KINETICS OF ALUMINUM OXIDE CERAMICS WITH AN ADDITIVE OF EUTECTIC COMPOSITION

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Specifics of sintering of ceramics based on aluminum oxide with a eutectic additive are studied. It is shown that the sintering process proceeds in two stages: before liquid-phase formation in the system the main mechanism controlling sintering is rearrangement of the particles of the high-melting phase; after the liquid-phase formation in the system the main kinetic process is dissolution-precipitation. The main parameters controlling the kinetic process are the size of particles of the high-melting phase and the physicochemical characteristics of the eutectic melt.

Structural ceramics with a decreased sintering temperature are among the most promising materials in contemporary engineering. Such ceramics can be used to develop cutting tools for metal, wood, and soft mineral rocks, drilling tools, friction-pair bearings, lock fittings, and other products. The significance of the new types of ceramics based on aluminum oxide is undeniable. However, the mechanism of sintering of these materials in some cases remains unclear from the scientific point of view.

It is known that sintering in the presence of low-melting additives of eutectic composition can proceed in two directions. In the first case, the solid phase is insoluble in the liquid phase, and sintering takes place due to surface-tension forces. In this case, according to data of Kingery, Naidich, and Lavrinenko [1, 2], the amount of liquid phase in the system should be at least 25 – 30% (hereafter weight content is indicated) and, consequently, if we neglect the possible change in volume caused by the phase transformation from the solid to the liquid state, the amount of low-melting additive introduced into the system should be at least 25%. In the second case, sintering is a three-stage process that includes rearrangement of the solid-phase particles, dissolution with precipitation, and formation of a solid skeleton. These processes are usually not clearly separated in time and frequently occur simultaneously and affect each other. Dissolution and precipitation may be controlled both by the kinetics of a chemical reaction on solid/liquid interface and diffusion of the reaction products through the interface layer. Knowledge of the process that actually controls sintering makes it possible to identify the principal factors by which it is possible to control the properties of the produced materials and,

accordingly, produce ceramics with high-level properties. The sintering process was studied in this work for the purpose of identifying the main processes taking place in firing and the factors controlling these processes.

The investigated factors that had an effect on the kinetic process were the type of initial aluminum oxide used for ceramics production, the quantity of sintering and strengthening (partly stabilized zirconium dioxide) additives, and the sample molding pressure and method.

The study was based on the exponential equation relating the sample shrinkage $\Delta l/l$ to the process duration τ and temperature T [3]:

$$\Delta l/l = k \exp\left(-(E/RT)\right)\tau^{\,n},$$

where k is the preexponential factor; E is the apparent activation energy; R is the universal gas constant; n is the sintering index.

The mechanism of the sintering process was inferred from the apparent activation energy and the sintering index. The experiments consisted in a series of consecutive firings in the temperature interval of 1523 – 1723 K with a step of 50 K, and 10 samples were investigated at each point.

The effect of the type of aluminum oxide on the kinetic process was studied on samples whose initial material was GLMK alumina pulverized by wet grinding for 24 and 48 h (GLMK-1 and GLMK-2, respectively) and aluminum oxide produced from industrial aluminum hydroxide ($Al_2O_3 - G$). The molding pressure in all cases was 200 MPa, and the amount of sintering additive was 4%. The experimental results are shown in Table 1. It can be seen that regardless of the initial material, the index n decreases as the firing temperature increases. The main sintering mechanism for the

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TABLE 1

Firing tempera-ture, K	Sintering index of ceramics based on				
	Al_2O_3 – G containing sintering additive			GLMK-1 containing 4% sintering additive	GLMK-2 containing 4% sintering additive
	2%	3%	4%		
1523	0.16	0.12	0.10	0.31	0.30
1573	0.15	0.10	0.10	0.31	0.24
1623	0.11	0.07	0.07	0.25	0.22
1673	0.11	0.07	0.07	0.10	0.10
1723	0.10	0.07	0.06	0.07	0.05

TABLE 2

Firing tempera-ture, K	Sintering index of ceramics* based on					
	Al_2O_3 – G containing sintering additive				GLMK-1 containing 4% sintering additive	GLMK-2 containing 4% sintering additive
	2%	3%	4%	5%		
1523	0.13	0.13	0.11	0.12	0.30	0.30
1573	0.13	0.12	0.11	0.10	0.25	0.24
1623	0.11	0.11	0.09	0.07	0.27	0.21
1673	0.09	0.09	0.07	0.06	0.11	0.08
1723	0.06	0.06	0.04	0.03	0.05	0.06

* In all cases 20% PSZD was introduced.

studied materials is a dissolution-precipitation process controlled by diffusion. This is corroborated by the correlation of the sintering indices with values of n for this process cited in the literature [2, 4, 5].

The solubility of the solid phase in the liquid phase is confirmed by the fact that dense ceramic materials can be produced from compositions with up to 5% low-melting additive, which is obviously insufficient for sintering ceramics with an additive in which the solid phase is insoluble. Passage to a more active raw material produces a significant decrease in n, other conditions being equal (firing temperature and duration).

Thus, the use of more active and disperse aluminum oxide powders significantly decreases the effect of the time factor, and therefore, the most significant factors are the particle size of the high-melting phase, the system viscosity, the boundary-layer thickness, and the concentration gradient of the soluble component on the convex and concave surfaces. The quality of the sintering process and, accordingly, the quality of the ceramics depend on the above group of factors. These parameters determine the possibility of sintering at decreased temperatures. Consequently, the most efficient methods for activation of sintering are reduction of the solid-phase particle size and use of eutectics that form melts with minimum viscosity and rather high surface tension. The

deceleration of the process at increased temperatures is probably related to a decrease in the motive force (the concentration gradient of the components of the soluble solid phase on the convex and concave surfaces). Moreover, the system reaches virtually theoretical density, which results in cessation of shrinkage.

The effect of the strengthening additive of partly stabilized zirconium dioxide (PSZD) on the sintering is reflected in Table 2. Introduction of PSZD does not change the sintering mechanism. The sintering indices of the materials containing PSZD and the materials without PSZD turn out to be equal within the limits of the error in determining the sintering index for the corresponding temperatures. Similarly to the materials not bearing PSZD, the index n decreases when the aluminum oxide is changed to a more active and more disperse variety.

One of the factors that has a significant effect on the sintering process is the quantity of eutectic melt present in the material during firing. The initial material was Al_2O_3 – G, and the quantity of the additive was varied from 2 to 5% (see Tables 1 and 2). The materials bearing 2 to 5% sintering additive exhibit a decrease in the index n with increasing temperature, which is probably related to a decreasing motive force. All sintering indices are within the limits typical of a dissolution-precipitation process controlled by diffusion and, consequently, this is the main process that limits the rate of ceramics sintering.

An increased quantity of the additive produced a certain decrease in n in series with T = const. This proves that a higher content of the additive and, accordingly, a greater quantity of the liquid phase in the system make it possible to intensify the process at lower temperatures. In doing so, compaction and shrinkage virtually cease in the temperature region of 1723 K. The indices n for the considered temperature interval indicate a common sintering mechanism for the materials containing 2 – 5% eutectic additive.

A most significant parameter of the sintering process is the apparent activation energy. Since the sintering rate under isothermal conditions decreases with time, the value of E should be computed for the moment corresponding to the time of attainment of the same shrinkage value for different firing temperatures. However, this moment is virtually unattainable for the considered materials. Therefore, the method of nonisothermal sintering [3, 6] was used to calculate the apparent energy.

To analyze sintering under nonisothermal conditions, the reaction rate equation that relates the relative shrinkage z to the temperature was used:

$$dz/d\tau = zk \exp\left(-(E/RT)\right)(E/RT^2),$$

where $z = l - (\Delta l/l)/(\Delta l/l)_{max}$ ($(\Delta l/l)_{max}$ is the linear shrinkage at the maximum firing temperature).

TABLE 3

Semidry-molding pressure, MPa	Additive content, %		Activation energy, kJ/mole	
	strengthening	sintering	E_1	E_2
Ceramics based on $Al_2O_3 - G$				
50	20	4	155	208
100	20	4	186	233
400*	20	4	358	236
50	20	1	150	201
50	20	2	160	244
50	20	3	144	210
50	20	5	150	205
200	30	4	215	268
Ceramics based on GLMK-1				
200	20	4	210	416
Ceramics based on GLMK-2				
200	20	4	202	416
Ceramics based on GN-1				
200	20	4	220	450

* Hydrostatic molding.

Fig. 1. Apparent activation energy of sintering of ceramic samples of composition $Al_2O_3 - G$ + 20% PSZD + 4% eutectic additive: *1* and *2*) semidry-molding pressure of 50 and 100 MPa, respectively; *3*) hydrostatic-molding pressure of 400 MPa.

In linear coordinates this equation has the form

$$\ln(-\ln z) = \ln(-(k/v)) - E/RT,$$

where v is the furnace heating rate.

The results obtained are shown in Table 3. Figure 1 shows an example of calculating the apparent activation energy for samples of composition $Al_2O_3 - G$ + 20% PSZD + 4% eutectic additive. As can be seen, sintering in each case occurs in two stages: the activation energy of the first stage E_1 varies over a wide range (from 140 to 360 kJ/mole) depending on the molding pressure. For a constant molding pressure and a varying quantity of the sintering additive and various initial materials, the value of E_1 remains constant. Hence, the process kinetics in the first stage depends exclusively on the molding pressure, i.e., on the geometric shape of the contact zone of the particles in the sample. An increase in the molding pressure results in denser packing of the particles, which complicates their movement in microvolumes in the early stage of sintering and causes an increase in the apparent activation energy. Thus, sintering starts with a rearrangement of the particles.

The activation energy of the second stage of the process depends on the dispersion of the initial aluminum oxide and does not depend on the molding pressure or the quantity of introduced sintering additive in the considered amounts. Thus, all the materials based on $Al_2O_3 - G$ have an activation energy of 228 ± 20 kJ/mole; in changing over to other types of initial material, the value of E_2 changes significantly. Therefore, the activation energy E_2 relates directly to the dissolution-precipitation process. The energy barrier that the system has to overcome is probably determined by the physicochemical prehistory of the initial material: passage to a more active and disperse material fosters a decrease in this
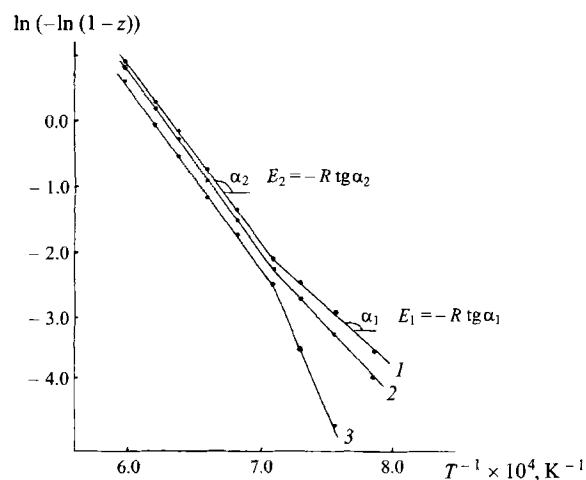
barrier and, accordingly, a more active process at decreased temperatures.

The following feature typical of all the investigated materials should be noted: the transition from one mechanism to the other takes place at the same temperature, regardless of the type of material used. The transition point corresponds to the temperature of appearance of the liquid phase in the multicomponent system. The transition temperature is 1413 ± 5 K, which is established by the results of the calculations of the process of nonisothermal sintering (Fig. 1).

Thus, the size of the particles of the high-melting phase and the quantity of the sintering additive have a greater effect on the sintering of the considered materials than all the other factors. Kinetically the process occurs in two stages: up to the moment when the liquid phase is formed in the system the main mechanism controlling sintering is rearrangement of the particles of the high-melting phase; after the liquid phase is formed in the system, dissolution with precipitation becomes the main kinetic process.

REFERENCES

1. W. D. Kingery, *Introduction to Ceramics* [Russian translation], IL, Moscow (1962).
2. V. N. Eremenko, Yu. V. Naidich, and I. A. Lavrinenko, *Sintering in the Presence of a Liquid Metallic Phase* [in Russian], Naukova Dumka, Kiev (1968).
3. *A Practical Course in the Chemical Engineering of Ceramics and Refractories* [in Russian], Stroiizdat, Moscow (1972).
4. O. H. Kwon and G. L. Messing, "Kinetic analysis of solution-precipitation during liquid phase sintering of alumina," *Am. Ceram. Soc.*, **73**(2), 275 – 281 (1990).
5. N. A. Makarov, E. A. Bad'ina, and E. S. Lukin, "Specifics of sintering of corundum ceramics with additives of eutectic composition," *Steklo Keram.*, No. 8, 15 – 17 (1998).
6. V. A. Ivensen, *Phenomenology of Sintering* [in Russian], Metallurgiya, Moscow (1985).